FINAL REPORT
to
the Joint Oceanographic Institutions, Inc.
March 1994

Cynthia Jane Decker
Office of Naval Research

In the time I have been with JOI, I have worked exclusively for the Office of Naval Research Environmental Quality Programs. These programs and many of my activities have been described in various progress reports that have been submitted to JOI but I will summarize them here.

The ONR Environmental Quality Programs were initiated in summer 1992. The programs were created as a three-year, $13 million/year effort. There are three programs included in the overall plan:

1) the Marine Environmental Quality program (MEQ), focused on the fate and effects of toxic substances in marine estuaries and near-coastal systems;
2) the Environmentally Sound Ships program (ESS), focused on treatment and elimination of shipboard waste streams;
3) the Marine Mammal program, focused on the effects of low-frequency active acoustic signals on the physiology and behavior of whales, dolphins, sea lions and seals.

Most of my activities the last year have been focused on the first two programs. The third program has been developed and managed by Dr. Dan Costa and Dr. Terrie Williams of ONR. My involvement in it has been minimal to nonexistent.

All of the decisions for the MEQ and ESS programs were made by the ONR Environmental Quality Coordinating Committee (EQCC). This group is chaired by Dr. Ronald DeMarco, director of the Chemistry Division. I am vice chair of the committee. The other members consist of scientific officers from all of the old 6.1 research departments within ONR, reps from the 6.2 and 6.3 environmental research programs and a rep from the Naval Research Laboratory.

The MEQ program was conceived of as a single, integrated program. A Broad Agency Announcement for the program went out in August 1992. Preproposals were received and reviewed in October and requests for full proposals went out in November. At the time my work for JOI began, the full three-year proposals had been received. These proposals were reviewed, funding decisions were made and the results were communicated to the principal investigators by mid-April 1993. Attachment A to this report includes brief descriptions of the thrust areas covered in this program.

Once the funding was disbursed, I planned and coordinated a workshop in July 1994 to which all of the MEQ-funded investigators, members of the EQCC, and representatives from several other federal agencies were invited. The purpose of this meeting was to bring the scientists together with the ONR program managers to discuss the common objectives of the program and plan coordinated field activities. Attachment B to this report is a copy of the

workshop summary. Another workshop for this program will be held in September 1994. At this time, the investigators are expected to report to the ONR program managers and representatives from other federal agencies on the results of their first year's research.

The Environmentally Sound Ships Program was developed in an manner different from that of the MEQ program. This program is tightly coordinated with the Naval Sea Systems Engineering Command (NAVSEA) as there is already a large program there which is addressing many of the technical solutions to shipboard waste problems. The EQCC called for ideas for research initiatives from within ONR. We received a number of proposals from ONR scientific officers as well as from the Navy research labs. A number of these were selected to be presented to the ONR EQCC, representatives from NAVSEA, and the ONR Research Advisory Board. These participants scored and ranked the proposed initiatives; funding decisions were based upon these. Projects funded under the ESS program include:

1) Shipboard waste conversion;
2) Membrane technology;
3) Non-emission refrigeration;
4) Environmentally-sound coatings;
5) In situ, real time sensors;
6) Clean naval power plants

Attachment C contains a brief description of these.

Other activities in which I participated which are relevant included the presentation of briefings on the ONR environmental quality programs at many of the ONR Ocean Sciences Department site visits in 1993. These included Scripps Institute of Oceanography, University of Washington, Oregon State University, Woods Hole Oceanographic Institution and University of Hawaii. I provided information on all of the ONR EQ programs but concentrated particularly on the MEQ program in these presentations. I also reviewed proposals for Ocean Sciences in the Young Investigator, the ASSERT and the DEPSCOR Programs.

In addition to activities within ONR, I was able to assist first CDR Scott Sandgathe and then Dr. DeMarco in representing the Office of Naval Research in processes elsewhere in the Navy having to with environmental issues.

CDR Sandgathe and I participated in the Environmental Quality "Roundtable" process in the spring of 1993. This process consisted of bringing together reps from the Systems Commands and several other activities to develop the science and technology (6.1-6.3 research) requirements. The process was chaired by N45 and overseen by N91. Once requirements were established in Roundtable 1, ONR was expected to provide a response in the form of an "investment strategy" including current and proposed programs. This response was presented at Roundtable 2. The purpose of this was to provide the resource sponsors for S&T with an overview of ongoing programs at ONR and enable them to provide a very general critique of ONR's research "investments" in this area. This process is being repeated for all Navy mission areas; environmental quality was the first area to undergo the process. My main responsibility in this activity was to assist in the preparation of the ONR presentation. I collected and wrote up information on relevant research programs in the Army, Air Force, DoD, other federal agencies and industry.

I also shared ONR representation with CDR Sandgathe and then Dr. DeMarco on the

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March 21, 1994

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RE: N0O014-93-1-0372, Final Report

Dear Sir/Madam:

Enclosed please find one copy of the final report for the above referenced grant.

If there are any questions, please don't hesitate to call.

Sincerely,

Monique C. Bryant

Monique C. Bryant
Contracts Associate

Enclosures

cc: E. Kappel
M. Fitzgerald
G. Hopson

Navy environmental quality working group (EQWG). This group is chaired by N45 and oversees the development of the Navy research and development requirements and programs. It is somewhat similar to the EQ Roundtable except that it covers all R&D from 6.1 through 6.7. I also participated in a subcommittee charged with coordinating and reconciling four separate lists of Navy EQ requirements which have been generated over the last couple of years, including:

1) the EQ Roundtable;
2) the CINC Combined Requirements;
3) the Ship Logistics Requirements, Goals and Objectives;
4) the Tri-Service Environmental Quality R&D Strategic Plan

The Tri-Service Plan mentioned in the previous paragraph was another project with which I became involved. This Plan originated out of the tri-service Project Reliance which was developed a few years ago as a way of coordinating the research done at military labs and avoiding duplication of effort. Environmental quality falls under the jurisdiction of the Reliance Joint Engineers Panel along with environmental effects and civil engineering. There are seven subareas in environmental quality. Numbers in parentheses indicate the service which has the lead in the area (A-Army, N-Navy, AF-Air Force):

1) Installation Restoration (A);
2) Noise Abatement (A/AF);
3) Pollution Prevention (A/N/AF);
4) Base Support (A);
5) Atmospheric Compliance (A/N/AF);
6) Global Marine Compliance (N);
7) Terrestrial and Aquatic Assessment (A)

The Tri-Service Plan was conceived of as a way of coordinating all service 6.1-6.3A research efforts, whether intramural or extramural. A different means of categorizing the research was proposed for this, however, and the Strategic Plan is divided up into four "pillars"

1) Clean-up
2) Compliance
3) Pollution Prevention
4) Conservation

The Strategic Plan contains a list of R&D requirements as promulgated by the "user" community. A second section, the bulk of the Plan, contains a series of "roadmaps" which illustrate the coordination of programs from 6.1-6.3A and through time. The programs are laid out as fitting into thrust areas which are defined as clusters of related requirements. The third section of the Plan is a collection of detailed write-ups on the research programs outlined in the roadmaps, including the requirements met, the R&D performer, the technical problem addressed and the impact the solution will have on the services. The first version of this Plan was released in January 1993. In December 1993, a complete revision of the Plan commenced. It is expected that a rough draft of this second version will be completed by June 1994.

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Finally, in the course of developing the ONR environmental quality programs, it was necessary to have some idea of what EQ research was being supported by other funding agencies in the federal government. During my time with ONR, established and maintained contact with a variety of offices having similar interests which are responsible for research programs. These include the Office of Research and Development of the Environmental Protection Agency; the Chesapeake Bay Toxics Program, the Coastal Ocean Program, the National Status and Trends Program and the National Sea Grant College Program in the National Oceanic and Atmospheric Administration; the US Fish and Wildlife Service and the US Geological Survey in the Department of the Interior; and the Office of Environmental Research and the Office of Demonstration, Testing and Evaluation in the Department of Energy.

In conclusion, let me say that it has been an extremely good fourteen months working at the Office of Naval Research through the aegis of the Joint Oceanographic Institutions, Inc. I have had nothing but good experiences. I have particularly enjoyed working with Dr. Rick Spinrad, Dr. Ron DeMarco and CDR Scott Sandgathe at ONR. It has also been a pleasure to deal with Ms. Penny Peters, Ms. Lynne Claflin and Ms. Linda Hare from JOI. I hope that both of these organizations have been satisfied with the work I have done for them.

Attachment A 3/10/94

Office of Naval Research
Environmental Quality Programs

6.2 (basic) RESEARCH

MARINE ENVIRONMENTAL QUALITY

Fate and effects of toxic substances in marine harbors, estuaries and near-coastal environments.

Thrust Areas

Sediment-Water Exchange FY93-$1392K, FY94-$1219K, FY95-$1103K

Studies of sediment transport dynamics and the physical and biological mechanisms affecting the flux of contaminants into and out of marine sediments.

Chemical Speciation and Phase Transfer FY93-$821K, FY94-$805K, FY95-$781K

Studies of trace metal cycling in the water column and biofeedback mechanisms affecting concentrations.

Bioavailability FY93-$853K, FY94-$801K, FY95-$628K

The uptake and metabolism of contaminants in marine organisms and the mechanisms by which this occurs.

Bioremediation and Novel Consortia FY93-$690K, FY94-$674K, FY95-$600K

A study of the biochemical mechanisms by which natural microbial consortia chemically degrade toxic organic compounds in marine sediments.

Ecotoxicology FY93-$334K, FY94-$345K, FY95-$345K

Examination of the effects of chronic, sublethal levels of toxic contaminants on marine food webs and modelling of the effects of pollution on marine populations.

In Situ, Real Time Sensors FY93-$210K, FY94-$200K, FY95-$223K

Fluorescent and fiber optic methods of sensing toxic chemicals in seawater.

Attachment B

OFFICE OF NAVAL RESEARCH

Marine Environmental Quality Workshop
19-20 July 1993
Airlie, VA

INTRODUCTION

Operations of the Department of Defense must be in compliance with federal, state and local environmental regulations. In addition, military operations in foreign locations may be constrained by current and future environmental regulations imposed by the host countries. Accordingly, the Navy is addressing these concerns by initiating broadly-based environmental quality programs. As part of this initiative, the Office of Naval Research has developed research programs to identify the basic science required for: (1) identification and removal of toxic substances from marine environments occupied by Navy ships and (2) development of environmentally-safe operations on these ships.

The Marine Environmental Quality Program addresses the first of these objectives. The thrust of this program is to increase the fundamental understanding of processes controlling inputs, fate and effects of toxic substances in estuarine and nearshore environments. Technical questions focus on the dispersal and distribution of contaminants in the sediment, water column and across the sediment/water interface; and on the effects on/by the natural systems of/on these substances.

The purpose of this workshop was to bring together the funded principal investigators to share information about proposed research, define the specific goals of the program, and to foster the coordination and collaboration of research efforts. There are several broad thrust areas covered by the program and a working group was convened corresponding to each one. These are:

(1) sediment-water exchange
(2) chemical speciation and phase transfer
(3) bioavailability
(4) bioremediation and toxicology

RESULTS OF WORKSHOP DISCUSSIONS

The chairs of the working groups were given guidance that asked them to focus their discussions to provide the following:

1) Four to six research issues considered as "most pressing" by the group
2) Anticipated accomplishments in the area covered by the group, including
   - what will be learned over the next three years
   - what is the importance/impact of that knowledge for harbor environmental quality
3) Identified research opportunities/issues after FY95 (and why they are important)
4) Opportunities for collaboration with other groups, e.g. sharing materials, sampling expeditions/access to sites, etc.

The results of these discussions were taken from the documents prepared by the working groups and submitted at the end of the workshop.

I. Major Research Issues

Sediment-Water Exchange

A. Broad Issues

1. What processes control the fate of chemicals, contaminants and metabolites within the benthic boundary layer (water column scale - meters; sediment scale - centimeters)?

2. What are the rates of transformations among major compartments (e.g. water column, sediment, solutes, solids)?

3. What are the important spatial and temporal scales over which these processes act?

4. How can we predict the ultimate fate (chemical, biological and geological transformations) of chemicals at the sediment-water interface in nearshore environments?

B. Specific Issues

1. What is the relative importance of solution-phase transport processes within sediments and across the sediment-water interface?
   - diffusion (complexation, speciation, molecule-specific)
   - bioirrigation (burrow wall permeability)
   - wave pumping (interaction with bottom roughness)
   - ground water (osmotic pressure differential, advection)
   - physical resuspension/entrainment

2. What is the relative importance of solids transport

processes within sediments and across the sediment-water interface?
- bioturbation (diffusive, non-local)
- physical processes (waves, currents)
- resuspension, deposition, burial
- mass movement
- anthropogenic processes (ships, dredging, trawling)

3. What is the relative importance of transformation processes between solutions and solids?
- redox reactions
- organic matter transformation (creation/destruction of living tissue)
- sorption/desorption (biological and physical)
- biogenic matter dissolution/precipitation
- inorganic dissolution/precipitation
- speciation/complexation

Chemical Speciation and Phase-Transfer

1.What are the processes that control chemical speciation and, thus, the behavior of contaminants in coastal environments? Specific areas highlighted include:
- role of colloids
- organic complexation
- redox processes
- solid phase speciation

2. What is the relationship between chemical speciation of toxic contaminants and their biological uptake and resulting impacts?

3. What are the basic mechanisms underlying these processes and the rates at which they occur?

4. How can this basic understanding of these processes be used to generalize our findings to a variety of coastal environments in order to predict the effect of contaminants on coastal ecosystems?

Bioavailability

A. Broad Issues

Bioavailability refers to the accessibility of material to uptake by biota. While physical inaccessibility can explain lack of availability, usually bioavailability is considered to be controlled by the chemical nature of the pollutant. Pollutants in the environment are divided into the following three sub-pools: 1) the bioavailable pool is the fraction of a pollutant that is in a chemical species which can be directly absorbed by an organism; 2) the potentially-available pool consists of material in a chemical form that can be converted to the bioavailable form by either the organisms or the environment, within time scales of environmental concern; 3) the non-bioavailable pool is that fraction of a pollutant that cannot be accessed by organisms on time scales of

interest to environmental managers.

1. The bioavailable species must be identified. One or more chemical species may be bioavailable. This speciation question is one that is dependent on both the organism and pollutant. The nature of the biological uptake process must be understood before identification of absorbable species can be made. This uptake process can vary across biotic taxa and with organismal physiology.

2. Interconversions among bioavailable, potentially-bioavailable, and non-bioavailable species must be understood. There is a reservoir of potentially-bioavailable material that represents the capacity of an environment to provide bioavailable pollutant. This capacity will depend on a number of environmental and biological conditions.

3. The context of environmental cycling of the pollutant must be understood. Different sources of pollutants may provide inputs that vary in their bioavailability. Likewise, the non-biotic sinks for pollutants may convert potentially-bioavailable material into forms that are not likely to become bioavailable on environmentally-relevant time scales.

B. Specific issues

1. Develop analytical methods and sensors that measure the bioavailable species and potentially-bioavailable pools to provide tools with which to make necessary measurements in field and lab situations.

2. Determine the limiting factors controlling flux from the potentially-bioavailable pool to organisms for particle-associated pollutants, with emphasis on both metals and organic compounds in sediment systems.

3. Determine rate-limiting factors controlling flux from the potentially-bioavailable pool to organisms for dissolved pollutants with emphasis on metal-phytoplankton interactions.

Bioremediation

1. Characterize novel, anaerobic metabolisms of selected contaminants. Characterization will include assessment of persistence and fate of hydrocarbons, chlorinated aromatics, munitions compounds and metals. This information can provide the basis for future exploitation and remediation purposes.

2. Characterize impacts of contaminants on trophic relationships and population dynamics within benthic communities. This includes experimental and modelling analyses.

3. Develop and evaluate the efficacy of molecular biological

approaches to bioremediation and assessment of pollution stress in marine ecosystems.

II. Anticipated Accomplishments

Sediment-Water Exchange

1. Quantifications of the roles of bioirrigation, wave pumping, physical shear and diffusion processes in the exchange of solutes across the sediment-water interface and within the sediment bed for a range of nearshore environments.

2. Quantifications of the roles of bioturbation (including biodeposition and biosuspension), physical reworking (due to waves and currents), and interactions of these processes in resuspension, deposition and particle residence time in an active surface-mixed-layer for a range of nearshore environments.

3. Identification of forms, mechanisms, rates of transformations between solute and solid phases for some chemicals, contaminants and metabolites (metals, PAHs, PCBs, nutrients) within the benthic boundary layer region.

4. A better understanding of the relative importance of biological versus chemical versus physical processes in governing the transport and fate of contaminants in nearshore benthic environments.

Chemical Speciation and Phase-Transfer

1. Validation of experimental methodologies through intercalibration (e.g. colloid characterization, metal complexation). Agreement between differing methodologies will provide a database which is not simply operationally defined and can therefore be related to fundamental chemical properties.

2. Establish the role of colloids in transport and bioavailability of contaminants. this will have an important impact on the fate and toxicity of contaminants.

3. The first determinations of dissolved, colloidal and particulate concentrations of specific individual PCBs and PAHs in coastal environments. This will enable us to understand the behavior and bioavailability of hydrophobic organic compounds.

4. Determine the impact of toxic metals (e.g. Cu, Cd, Zn) on natural phytoplankton assemblages.

5. Identify sources, sinks, binding constants and concentrations of metal-binding organic ligands. Evaluate their role in controlling bioavailability and solution-particle interactions. The findings in 4 and 5 will enable regulators to make informed decisions about acceptable levels of these metals in

coastal environments.

6. Identify the principal scavenging mechanisms for trace contaminants in selected estuarine environments, e.g. phytoplankton uptake versus abiotic adsorption processes.

7. Impact of sulfide minerals on the bioavailability of contaminant metals associated with anoxic sediments.

8. A new understanding of photo-redox reactions of Cu(II) complexes with organic ligands and the roles that these reactions play in modifying Cu speciation. This understanding will enable decision-makers to better assess the exposure levels of marine organisms to the most toxic forms of copper.

Bioavailability

1. Polyaromatic hydrocarbon (PAH) cycling and models for water column and sediment (northeastern U.S.).

2. Metal-phytoplankton interaction models, including identification of bioavailable and potentially-bioavailable species and their interconversions.

3. Role of pollutant-colloid associations as a significant vector in pollutant cycling.

4. In situ sensors for various heavy metals.

5. Analytical method and field determinations of potentially bioavailable pools of pollutants in sediments based on organismal digestive strategies.

These accomplishments will provide the Navy with a new ability to assess the status, or "health," of nearsnore environments, as well as the ability to elucidate pathways of pollutant cycling that will allow better design of the Navy nearshore environment interface. Both will be necessary to understand the impact of Navy operations on nearshore biota. In other words, there will result both new operational capability and a foundation of more focussed research on specific environmental problems.

Bioremediation

1. The investigators will gain information on the biodegradability of different hydrocarbon classes, the specific microbial processes which cause them to degrade, and the effect of other contaminants on the biodegradation of compounds within mixtures of waste.

2. This research will result in experimental and predictive models for the effects of certain contaminants on selected populations, which can be applied to other populations and contaminants.

3. The investigators will have developed rapid and accurate molecular biological means for characterizing ecosystem stress, detecting biodegradative capability, and metals sequestration.

III. Long-term research opportunities (beyond 1995)

Sediment-Water Exchange

1. Examination of processes and mechanisms that control sediment microstructure and microbial composition.

2. Incorporation of biogeochemical processes into estuarine circulation models to develop a predictive, whole-ecosystem model.

3. Examination of other solids and solution transport mechanisms such as mass movement, degassing, anthropogenic processes such as dredging and trawling, and groundwater inputs.

4. Examination of the flux of contaminants and early diagenesis within environments that are predominantly coarse-grained, and the effects of fine-grained material on bed response processes in these environments.

Chemical Speciation and Phase-Transfer

It is anticipated that the emphasis on basic processes will continue after fiscal year 1995. Thus, logical extensions of the research issues discussed above very likely will be carried out at that time. In addition, the following development is foreseen. Carry out a multidisciplinary study by different investigators ant two or three coastal sites to comprehensively study the coupling of important processes that regulate the fate and effects of toxic contaminants. This study will provide the basis for an overall conceptual model for the behavior and impact of these contaminants and will provide the basis for quantitative predictive models. Sites will be selected where physical processes can be well characterized so that findings can be incorporated into a comprehensive physical, chemical, and biological model.

Bioavailability

1. Modelling efforts in environmental cycling and biotic impacts of pollutants. These models will combine environmental processing with toxicological studies to allow integrated impact studies. Validation of these models will be possible with field studies using both the methods and results of the currently-funded work.

2. Specific processes not addressed in the current program include photochemistry of organic pollutants, air-water exchange, intracellular biomarkers and the bioavailability of lipophilic pollutants to bacteria.

3. Technology transition - sensor implementation in the field.

Bioremediation

1. Examine the biochemistry and genetics of anaerobic biodegradation in order to gain insight into the factors controlling the rate and extent of contaminant degradation. The information obtained has the potential to allow controlled manipulation of the biodegradative process; to expand the capacity for degradation under anaerobic conditions by construction of new biodegradative pathways; and to increase our understanding of the natural anaerobic biodegradative processes.

2. Develop models for predicting the environmental, chemical and physiological constraints to biodegradation. Such models will include information on the toxicology of the contaminants, the impact of bioremediation options and a quantitative evaluation of the health of harbor and nearshore ecosystems.

3. Carry out a field study for the purpose of testing our ability to predict ecosystem effects and implement appropriate bioremediation strategies.

4. Provide the scientific basis for the development of specialized environmental sensing technologies for the real time collection and analyses of biologically pertinent data.

IV. Potential for Collaborations

Sediment-Water Exchange

In order to facilitate collaboration, the working group produced a matrix relating investigator projects to the major research issues identified above, a summary of the major objectives/approaches that will be employed in each program, and a compilation of field schedules for each program (see appendix)

Chemical Speciation and Phase-Transfer

1. Moffett/Brand, Bruland/Hudson, Sunda/Huntsman and Donat/Burdige - intercalibration of chemical speciation techniques and characterization of phytoplankton metal interactions in a bloom.

2. Gill/Santschi/Benfield, Buessler/Gschwend, Bruland/Wells and Weber-Shirk/Jirka/Lion - intercomparison of methods for the isolation of colloidal material.

3. Donat/Burdige and Morse - pore water and solid phase speciation interactions.

4. Donat, Faust, and Moffett - photochemistry of isolated natural organic ligands.

Bioavailability

1. Metal speciation in the water column will have an important and close tie with bioavailability of metals to plankton. Biotic and abiotic processes have major impacts on metal speciation, driving metals in and out of the bioavailable "window."

2. Colloid cycling studies will need to interface with bioavailability work, because of the possibility that colloids act as either sinks or sources for bioavailable pollutants. Especially close contact must be maintained on the issue of definition of colloids. The operational nature of their isolation and study leads to the probability that use of the term "colloid" by different research groups will lead to confusion about their real significance. Standardization of methods, to the extent possible, would be highly desirable.

3. Many groups have similar sampling needs, making for economies of sampling cost as well as the opportunity to gain important ancillary information on samples for the participating groups.

4. Lipophilic pollutant degradation by bacteria is an important theme in the bioremediation group. The group's work will be enhanced by an understanding of the bioavailability of these materials. Availability of these pollutants to macrofauna, which will be studied in the bioavailability group, will have some (though not complete) relevance to bacterial uptake.

5. The environmental cycling of pollutants will involve considerable work in sediments. Groups working on the movement of sedimentary materials will have obvious relevance to the study of bioavailability of sediment-borne pollutants.

6. Work relevant to sensor development is being carried out in the group focusing on bioremediation. Active contact and collaboration will be maintained with that group, in order to plan coordinated development work growing out of the research phase of the current MEQ program.

Bioremediation

1. The coordinated field study proposed post-1995 would be a unique opportunity in which all members of this group would wish to participate.

2. There is potential to interface with other groups of investigators developing techniques to measure metal speciation with the objective of assessing interactions between microorganisms and metals.

SUMMARY

The workshop opened with a plenary session in which summaries of current Navy environmental quality research and general ONR objectives for the program were presented. This was followed by two concurrent sessions in which the principal investigators gave presentations on their proposed research. After these, the participants met in working groups corresponding to the thrust areas. Two additional plenary sessions were held during the workshop: one at the end of the first day for presentation of preliminary conclusions of the working groups and at the end of the second day's session for final presentations by the chairs of the working groups.

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APPENDIX

STATEMENTS OF OBJECTIVES

INTERFACE DYNAMICS IN COASTAL ENVIRONMENTS

Richard Bennett

The physical fate of the organic and inorganic constituents of bottom sediments are greatly influenced by the local flow regime at the sediment-fluid interface. The magnitude and spatial distribution of ocean currents are primarily responsible for the initiation of sediment movement and, as the level of bad shear stress increases, the resuspension, dispersion, and transport of sediments. The hydrodynamics component of this interdisciplinary investigation will describe the first order forces responsible for the dynamics of seafloor sediments, the current field and associated bed shear stresses. This study will address and quantify, for selected coastal environments, the role of ambient and dynamic pore water pressures in marine sediment stability, strength change, effective stress state, and pore fluid gradients as a function of surface wave activity, sediment types, and environmental stresses.

The study will focus also on the importance of hydrodynamic driving processes near the sediment-water interface and take into account other driving forces where appropriate. A major effort will be to develop a fundamental model for vertical transport of resuspended fine-grained sediment and chemical constituents incorporating the dynamic effects of waves and pore pressures within the compliant bottom and including desorption/adsorption/resorption kinetics within the bad and the water column.

The research team will address the processes driving the diagenesis of constituents in the bad, their exchange at the interface, and their post-sedimentation-resuspension desorption/adsorption kinetics over selected time-scales under wave action. In Phase I of the study, the team will develop an integrated experimental design and strategy for model development and validation.

In Phase II of the study, the team will investigate diagenetic and water column fluxes of non-decaying and non-sorbing constituents in the presence and absence of wave loading. This phase will be followed by Phase III involving non-conservative materials. In Phase IV we will develop a vertical transport model for the constituents in the fluid phase as well as particulate phase, encompassing the entire shallow water column from the water surface down into the bed to depth.

The interface dynamics effort will provide current and shear stress values for use in the investigation of the behavior of sediments in the near-shore and coastal environment. These will be provided through application of a three-dimensional finite element hydrodynamic model developed for application to very large computational domains which encompass continental shelves and coastal estuaries. This model is unique in that it was specifically developed to efficiently generate highly accurate tidal constituent and storm surge data bases over global-sized domains. Errors introduced at the continental shelf are minimized

by utilizing computational grids which extend beyond the continental shelf into deep water where tidal boundary conditions are well-defined. This hydrodynamic model will provide input data to sediment transport and sediment composition models which will be used to investigate the movement of sediment as well as the microbiological, geotechnical, rheological, and microstructural properties of sediment as a partial function of the physical characteristics of the flow field.

Field measurements of ambient and dynamic pore water pressures, bottom pressures generated from surface waves, current speed and direction, water and sediment temperatures, and bottom photography will be conducted in selected sediment types (saturated and unsaturated silts, clays, and muds) to test and evaluate existing hydrodynamic and geotechnical models. The effort will be field and model evaluation intensive. The field data will provide ground truth for theoretical hydrodynamics (Scheffner), the viscous sublayer (Faas), dynamic geochemistry (Hulbert), and pore pressure dynamics (Bennett).

A benthic transport, integrated, hydrodynamic model will be attempted which will incorporate such parameters as the following: 1) particle size and mineralogy, 2) sediment accumulation rates, 3) compaction with release of pore waters, 4) pore pressures which may exceed hydrostatic pressure, 5) adsorption/ desorption/ resorption kinetics, 6) the development of sediment shear strength (controls the response of fine cohesive sediment to wave orbital velocities and advective mass sediment transport), and 7) porosity and permeability processes beyond the scope of this project, e.g. bioturbation, diagenesis,etc., also create substrate conditions which must be understood and quantified for incorporation into a benthic sediment transport model for some geological environments. It should be noted that muddy sediments adsorb much greater amounts of contaminants and organics than sandy sediments and that clay minerals possess large surface areas and have different cation exchange capacities than do non-clay minerals. These processes and properties and their variability must be understood numerically and statistically in terms of the associated geological environments and geographic settings.

A crucial missing link is the testing and verification of existing seafloor models and development of sophisticated numerical models is a quantitative data base with "ground truth" relating sediment properties and sediment types to environments of deposition, erosion, sediment transport, and geographic setting.

TRACE ELEMENT AND NUTRIENT CYCLING IN LOS ANGELES HARBOR

William Berelson
Kenneth Johnson
Kenneth Coale

In this proposal, we describe a project to study the anthropogenic and biogeochemical factors that control cycling of trace metals and nutrients between the water column and sediments in the coastal environment. This work will focus initially on the Los Angeles/Long Beach harbor system. Our goal is to make quantitative measurements of the major fluxes of trace metals (copper, zinc, cadmium, manganese and iron) and nutrients (ammonia, nitrate, phosphate and silicate) and gases (oxygen, carbon dioxide and 222-Rn) into and out of the harbor system. Our work will focus on the role of sediments and sedimentary fluxes of dissolved chemical species. These measurements will be used to develop a predictive model of chemical cycling whereby the magnitude of the anthropogenic contributions of dissolved metal and nutrient species within this area can be addressed.

THE ROLE OF CHEMICAL SPECIATION IN PROCESSES GOVERNING THE ENVIRONMENTAL FATE AND EFFECTS OF TRACE METALS IN ESTUARINE AND NEAR-COASTAL ENVIRONMENTS

Kenneth Bruland
Robert Hudson

The goal of our proposed research is to further the basic understanding of the chemical speciation of Mn, Fe, Cu, Zn, Pb, and Cd within the water column of estuarine environments. This includes characterizing biotic and abiotic processes which control the observed chemical speciation, as well as the effects of trace metal speciation on other processes such as plankton productivity and/or species composition and the particle reactivity and/or cycling of trace metals. The research will also address interactive and antagonistic effects among these trace metals. We will examine processes that fall within the two broad categories of environmental fate and environmental effects of trace metals in estuarine environments. The type of results we anticipate are essential basic inputs for models of the coastal marine environment. specific objectives are listed below:

I. Aqueous Chemical Speciation and Particle-Water Partitioning

A. Quantify and characterize organic complexation of trace metals in estuarine waters

i. Measure the total concentrations of trace metals and metal complexing organic ligands and the stability constants of metal-ligand complexes. This permits calculation of ambient free metal ion concentrations and the metal ion buffering capacity of the water.

ii. Investigate competition between metals for binding to organic ligands. It is important to quantify the extent to which changes in the concentrations of one metal affect another.

iii. Distinguish the contributions from allochthonous (rivers, sewage inputs, storm runoff) and autochthonous (plankton and sediment diagenesis) sources to ambient levels of organic ligands through quantifying the concentrations in each end member and across spatial and temporal gradients.

B. Quantify partitioning of trace metals with colloids

i. Quantify ambient concentrations of trace metals present in colloidal matter.

ii. Characterize the affinity of colloids for trace metals by determining the equilibrium constants for adsorption on colloids and the concentrations of metal-binding surface sites.

C. Characterize partitioning of trace metals to particles

i. Quantify ambient concentrations of trace metals present in small (0.2-5 um) and large (>5 um) particle fractions.

ii. Characterize the fraction of trace metals in plankton and in abiotic particles through the application of specific chemical leaches to particulate matter across spatial and temporal gradients in plankton abundance.

II. Interactive Effects of Trace Metals and Phytoplankton

A. Effects of experimental manipulation of trace metal concentrations in the field

i. Quantify plankton growth, primary production, major nutrient utilization, and species composition changes with and without addition of nutrient (Fe, Mn, Zn) or toxic (Cu, Cd, Pb) trace metals in incubations of ambient water samples on-site.

ii. Quantify the above listed parameters upon addition of synthetic chelators and scrbents in incubations of ambient water samples.

B. Quantify trace metal uptake kinetics by particles and by plankton

i. Using radiotracer additions and specific chemical leaches, measure uptake rates in incubations under bloom and non-bloom conditions.

ii. Using radiotracer additions and specific chemical leaches, measure uptake kinetics and equilibria for trace metal sorption onto abiotic particles.

THE ROLE OF DEPOSIT- AND SUSPENSION-FEEDING BENTHIC INVERTEBRATES IN THE TRANSFER OF CONTAMINANTS BETWEEN THE WATER COLUMN AND BOTTOM SEDIMENTS

Cheryl Ann Butman
Robert Wheatcroft

The broadest objective of this proposed research is to determine the dominant mechanisms whereby and rates at which fine particles are incorporated into marine sediments. Specifically, at what rates do deposit- versus suspension-feeding benthic invertebrate populations sequester fine-grained particles (to which contaminants are typically adsorbed) from the water column and retain them within the sediment bed, relative to the abiotic case? Our intent is to manipulate and test various combinations of hydrodynamical, sedimentological and biological parameters to determine the magnitude of 1) net accumulation of fine particles in sandy and reworked sediments relative to muddy sediments, 2) biodeposition by suspension-feeders relative to deposit feeders, and 3) vertical transport of sediment within the bed by deposit feeders.

This research seeks to obtain a more complete understanding of the effects of the two dominant feeding types of organisms in soft-sediment communities on fine-particle deposition and accumulation in the broad spectrum of sedimentary environments (i.e. erosional, depositional and reworked) that occur in estuarine and near-shore coastal areas. Specific hypotheses that will be tested during the course of this research are the following: 1) biodeposition due to suspension feeders in steady flows can result in substantial fine-particle accumulation in sandy areas, particularly if suspension feeders defecate within the bed, or if co-occurring deposit feeders can vertically transport the deposited material to "burial" depths within the bed; 2) in unsteady flows (tidal), fine-particle deposition and accumulation can be substantial due to deposit feeding (subsurface and surface) activity during slack water periods; 3) in unsteady flows (tidal), biodeposition due to suspension feeders may be substantial during flood and ebb periods.

AN EXPERIMENTAL INVESTIGATION OF THE INFLUENCE OF DIESEL FUEL ON THE FOOD WEBS OF TWO SEDIMENTARY COMMUNITIES

Kevin Carman

The primary objective of our proposed research is to determine the influence of diesel fuel on functional and structural attributes of salt-marsh benthic food webs. The food web that we will examine is the microbe-meiofauna-juvenile fish interaction, typical of Atlantic and Gulf-coast estuaries. We will test a number of discrete hypotheses concerning the influence of diesel fuel on various components/aspects of the food web.

Our second objective is to determine the potential for evolutionary response by members of this food web to chronically contaminated sediments. To accomplish this we will compare the response of the benthic food web in two salt marshes, one that has been chronically exposed to contaminants for decades, and another that is relatively pristine.

For each of the null hypotheses identified below, a two-sided alternative exists, e.g., the influence of diesel fuel may be either stimulatory or inhibitory. Stated differently, we are making no a priori assumptions concerning the influence of diesel fuel on the sedimentary food web. Hypotheses 1-3 will be tested using data from microcosm studies, and hypothesis 4 will be examined in laboratory experiments. Hypothesis 5, which relates to our second objective, will be examined by comparing experimental results from the two study sites.

General Null Hypothesis: Diesel fuel does not influence salt-marsh benthic food webs.

Null Hypothesis 1: Diesel fuel does not influence microbial activity.
Response variables: (A) Benthic microalgal activity as determined by incorporation of 14-C-bicarbonate; (B) Growth condition of benthic bacteria as determined by partitioning of 14-C-acetate into membrane and storage lipids.

Null Hypothesis 2: Diesel fuel does not influence grazing by meiofauna on microbial food resources.
Response variable: Grazing by meiofauna on microalgae as determined by radiotracer experiments.

Null Hypothesis 3: Diesel fuel does not influence the nutritional status of meiofauna.
Response variable: Relative quantity of lipid storage material in meiofauna as determined by nile-red assay.

Null Hypothesis 4: Diesel fuel dies not influence fish predation on meiofauna.
Response variable: Quantification of feeding intensity and

behavior as it relates to sediment contamination.

Null Hypothesis 5: Previous exposure to contaminants does not influence the sensitivity of the salt-marsh food web to diesel fuel.

Response variables: Comparison of dosage concentrations that cause significant response(s) by one or more components of the two food webs (one chronically exposed to contaminants, one pristine).

TRANSFORMATION OF HAZARDOUS WASTES, USING FOREGUT BACTERIA FROM THE BOWHEAD WHALE

A. Morrie Craig

The overall goal is to obtain bacteria from the bowhead whale foregut, which biotransform harmful environmental chemicals. The specific objectives are:

(1) to test whether bowhead whale (Baleana mysticetus) foregut and intestinal bacteria biodegrade, transform, or detoxify EPA's priority pollutants, especially nitrogen-containing compounds including trinitrotoluene, picric acid, and triazines

(2) to isolate and characterize these potentially beneficial bacteria from the bowhead foregut

(3) to optimize the conditions required for biotransformation of selected toxic chemicals by the isolated bacteria and

(4) to establish a bacterial culture collection for use by civil and chemical engineers to use for bioremediation applications, derived from the bowhead whale foregut bacterial populations.

These objectives address several research areas of interest to ONR, including the environmental fate, transformation, and degradation (including bioremediation) of substances in the listed categories; and characterizing the contributions of organisms or groups of organisms that regulate the fates of discharged substances.

EFFECTS OF SPECIATION ON SEDIMENT-WATER EXCHANGE OF METALS

John R. Donat
David J. Burdige

The specific aim of our proposed research is to determine the speciation of selected trace metals (copper, Cu and cadmium, Cd) in pore waters and determine the role that it plays in the sediment-water exchange of these metals in estuarine and near-coastal environments. Questions that we will have to address in examining this problem include:

(1) What is the speciation of dissolved Cu and Cd in pore waters and in bottom waters above the sediment-water interface?

(2) What relationship does sediment biogeochemistry have on the speciation of dissolved Cu and Cd in pore waters?

(3) What are the magnitude and direction (into or out of sediments) of Cu and Cd benthic fluxes?

(4) Does the speciation of dissolved Cu and Cd in pore waters influence the measured diffusion coefficients and benthic fluxes of Cu and Cd?

specific study sites for this project will be chosen within Hampton Roads (Elizabeth River estuary), the Chesapeake Bay proper, and the mid-Atlantic continental shelf. We chose these regions because sediments here show a range of trace metal and organic carbon loading (deposition) rates, and we hypothesize that these factors likely play important roles in affecting Cu and Cd pore water speciation and benthic fluxes. Comparative studies at these sites will be important in helping us answer the questions posed above.

PHOTO-REDOX REACTIONS OF COPPER COMPLEXES: EFFECTS ON COPPER SPECIATION AND OXIDANT FORMATION IN MARINE AQUATIC SYSTEMS

Bruce Faust

Objective 1. Quantify and provide a mechanistic understanding of the effects of structure on the photo-reactivity of Cu(II)/organic-ligand complexes representing the likely range of coordination environments experienced by Cu(II) in marine waters and in the intracellular aquatic environments of optically-transparent marine microorganisms.

Objective 2. Elucidate the mechanisms and quantify the structure-reactivity effects on the photolysis of Cu(II)-organic complexes as sources of Cu(II) and H_2O_2 in the aforementioned marine aquatic environments.

Objective 3. Identify, quantify, and understand mechanistic relationships between the photo-formation of Cu(I) and H_2O_2 from the Cu(II)-organic complexes.

INFLUENCE OF COLLOID AND PARTICLE ASSOCIATIONS ON XENOBIOTIC ORGANIC COMPOUND CYCLING IN NEAR-COASTAL WATERS

Philip M. Gschwend
Ken O. Buesseler

It is our overriding goal to enable the estimation of xenobiotic organic compound fates and effects in harbor and coastal seawater. To this end, we propose that much progress can be made if we: (1) develop the quantitative basis for evaluating the solution-colloid-particle distribution of these substances as a function of their physical-chemical properties and the characteristics of the solution/suspension, and (2) couple this "speciation" understanding with rate information for the colloidal phases and particle dynamics in such nearshore regions.

More specifically, our first goal is to evaluate the hypothesis that xenobiotic organic compounds are at sorption equilibrium in coastal seawater. We believe that previous efforts to establish that this is true have failed because: (1) specific individual compounds were not analyzed or modelled in each phase, but rather aggregate compound classes were examined exhibiting a range of partitioning properties (comparable to lumping all the metals into one solid-solution sorption coefficient); (2) the operationally defined solution phase contained sorbing materials in the form of colloids and this "cross-over" effect was not taken into account; and/or (3) some of the specific compounds under consideration included a substantial contribution from soot-bound molecules which were not free to participate in sorptive exchange. Thus our initial objective is to evaluate harbor and coastal seawater samples with these concerns in mind and thereby to develop an organic chemical "speciation" data set that can be used to evaluate whether thermodynamic properties of these contaminants are useful for estimating their fates and bioavailability.

Our second major goal is to combine our findings on organic chemical phase associations with closely related data quantifying colloid and particle dynamics obtained simultaneously for the same harbor/coastal region. This key step will enable us to calculate the influence of solid-phase dynamics on xenobiotic organic compound cycling in these nearshore waters.

METHODS FOR THE FLUORESCENT SENSING OF DIVALENT CATIONS AND SMALL MOLECULES IN SEAWATER

Richard P. Haugland
Michael A. Kuhn

Our goal is to develop optical indicators and test methods for the rapid and sensitive detection of pollutants that find their way into the marine environment, either through Naval activities or by other means. Early and rapid sensing of these pollutants, particularly in harbors and other environmentally-sensitive locations will permit a more rapid response to alleviate the cause of the pollution. We will create easy-to-perform tests that can use inexpensive instrumentation for the measurement. Our ability to adapt these reagents to unattended instrumentation and to use them on-board ship or in other remote locations should facilitate continuous or remote sensing of these potential environmental hazards.

Current methods for the measurement of marine pollutants usually require a sampling step followed by laboratory analysis that uses such techniques as atomic absorption spectroscopy (AA), ion-selective electrodes, high performance liquid chromatography (HPLC), or mass spectroscopy (MS). All of these techniques require expensive, often fragile instrumentation that is not very portable and that requires a skilled operator. Furthermore, the extraction and concentration steps that may be necessary to obtain the required sensitivity and selectivity can contaminate samples. It is our overall goal to produce tests that can, for instance, directly estimate the concentration of a pollutant by adding a few drops of a dilute, non-toxic indicator solution to a small sample of seawater. Some of our proposed tests will be designed to measure pollutants using an inexpensive hand-held fluorometer where excitation is by a simple light-emitting diode (LED). If required, many of the reagents that we propose can be adapted for use on a fiber optic bundle for direct detection of the analyte in seawater. Furthermore, we envision that the ability to measure the optical response in real-time using unattended equipment will permit the Navy to develop floating sensors for pollutants that can be monitored by satellite transmission.

Our intention is to develop analyte-selective fluorescent dyes and test methods that will give a rapid and reversible optical response on binding a target ion or molecule. Because of the diversity of potential marine pollutants, their varying concentrations and the possible situation where they may be encountered, it is expected that the contracting agency will provide additional guidance in specifying their expectations and priorities. When required, the scientific approaches described in our proposal will be modified to detect analytes other than those listed. Currently identified targets include cations (particularly Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, and Cs^{+}), polyaromatic hydrocarbons (PAH), pesticides and polychlorinated biphenyl (PCB) derivatives and water miscible and immiscible solvents.

The high sensitivity of fluorescence measurements should permit the direct measurement of trace contaminants in seawater by methods that will have minimal requirements for sample preparation or analyte separation. We will design indicators that will have a real-time, reversible fluorescent binding response. We will incorporate synthetic modifications to produce indicators that will have the appropriate affinity and selectivity for the analyte in the marine environment. In addition to being useful for measuring the pollutants dissolved in seawater, the reagents will be useful for the rapid qualitative and quantitative analysis of aqueous or organic extracts of marine life, suspensions, sediments, rocks, plants, soils and other samples. The same tests can be used to assess the success of pollution clean-up efforts.

The relatively short duration and limited funding of this grant will not permit full development of all of the research ideas that are presented in this proposal. We will solicit the guidance of the contracting agency in developing priorities. The primary objective of the proposed research is to develop as many of the priority reagents and complete tests that we will describe as possible and to ensure that these will have the appropriate sensitivity and selectivity for the analytes that have been identified as being of the greatest interest to the contractor. Molecular Probes would make these reagents and tests available to the Navy and to researchers through its established distribution network. We will likely defer internal development of the supporting instrumentation or would accomplish this through collaborators at other companies or institutions.

IN SITU PCR PROCEDURES FOR DETERMINATION AND ACTIVITY OF SPECIFIC GENES FOR AROMATIC POLLUTANT DEGRADATION IN MARINE WATERS AND SEDIMENTS

Robert E. Hodson

Global Objectives:

(1) To develop and optimize procedures for in situ PCR amplification and direct microscopic detection of specific genes in individual cells in natural populations of marine bacteria and other marine microorganisms

(2) To determine the distribution in seawater and sediments of natural marine bacteria possessing the target genes (TOL and NAH plasmids).

(3) To integrate the in situ PCR technique for gene detection in individual cells with existing in situ hybridization techniques for taxonomic identification of individual bacterial cells as a means of determining which species of bacteria in natural samples carry the genes for selected pollutant degradation processes.

Specific Methodological Objectives:

(1) To modify existing in situ PCR gene amplification technologies for use with bacteria, including specific strains and natural populations of marine bacteria, for detecting genes involved in the degradation of aromatic hydrocarbon pollutants in marine environments (toluene and naphthalene). Direct visual detection of specific genes in individual bacterial cells has not been demonstrated to date, although analogous techniques have been used successfully during the past two years to microscopically detect specific target genes in eucaryotic cells and human tissue preparations.

(2) To methodically determine which parameters are critical to successful in situ PCR in procaryotic cells in general and natural marine bacterial populations specifically. We expect critical parameters to include (but not necessarily be limited to) methods of cell collection and fixation; procedures for permeabilizing fixed cells to facilitate entry of the requisite enzymes, oligonucleotide primers, etc.; micro-scale geometry of running the polymerase chain reaction on microscope slides; temperature and chemical conditions during thermal cycling; retention of amplified DNA target sequences within individual cells; and methods for visualization of the amplified gene sequences.

(3) To determine the range of types of marine bacteria and eucaryotic microorganisms which are amenable to direct gene detection by in situ PCR and the degree of technique modification which will likely be necessary to optimize the initial detection techniques for use with various marine microbial species and various types of marine samples (seawater vs sediment; aerobic vs anaerobic environments; free-living vs attached microbiota, etc.).

(4) To develop and demonstrate the utility of combining the marine bacterial in situ PCR procedures that will be developed in this study with existing 16S rRNA probing techniques.

THE EFFECT OF METALS ON THE BIOTRANSFORMATION OF CHLORINATED AND NONCHLORINATED AROMATIC COMPOUNDS BY ANAEROBIC BACTERIAL CONSORTIA

Joanne M. Horn
Barbara Genthner

The primary goal of these investigations is to determine the effects of toxic transition metal ions (Cd(II), Cu(VI), Cu(II) and Hg(II)) commonly associated with hazardous waste on the anaerobic degradation of both simple (monochlorobenzoates and monochlorophenols) and complex (pentachlorophenol) haloaromatic compounds, as well as a toxic nonchlorinated aromatic compound, phenol. Specifically, the study is aimed at demonstrating the precise steps of a given biodegradative pathway that are subject to heavy metal inhibition. Further, we wish to define environmental conditions that anaerobic degradative bacteria would be expected to encounter under natural conditions. The overall toxicity of these metal ions to the anaerobic microorganisms under study is an initial objective that will permit determination of operant metal resistant mechanisms. Finally, estimation of the effects of anaerobic metal resistance on alleviation of metal-sensitive steps of (halo)aromatic degradation will be sought.

MECHANISMS AND FACTORS REGULATING THE UPTAKE AND TOXICITY OF HEAVY METALS IN PHYTOPLANKTON

Susan A. Huntsman
William G. Sunda

Our primary objective is to define the environmental factors and to understand the underlying physiological mechanisms that regulate the uptake and toxicity of copper, cadmium, and zinc in coastal and estuarine phytoplankton. A related objective is to use this understanding to predict or assess both the effects of trace metal toxicity in contaminated estuarine systems, and the role of phytoplankton in the particulate removal, transport and cycling of metals in estuarine and coastal waters.

DETECTION OF IN SITU GENETIC DAMAGE IN MARINE BACTERIA RESULTING FROM INTRODUCES XENOBIOTICS

Wade H. Jeffrey

The principle objective of this project is to develop a sensitive approach for defining the genetic/molecular response of marine bacteria to xenobiotics and to correlate that response with ecological changes in the microbial community. The bacterial response will be evaluated with concurrent measurements of genetic transcription and translation. Concomitant estimates of bacterial biomass and activity will be used to study the effect of pollutants on bacterial production and nutrient recycling in estuaries. The combined results will provide a detailed response of marine bacteria at the genetic level and the subsequent ecological effect which may result from the genetic stress.

The genetic effects of pollutants will be examined by determining whether xenobiotics induce the DNA damage repair mechanisms of marine and estuarine bacteria. We will monitor the expression of the regulatory gene (recA) for the bacterial DNA damage repair system (SOS System). To accomplish this goal we must: (1) establish the detection limits of recA DNA, mRNA and RecA protein the environment; and (2) examine the induction by xenobiotics of the DNA damage repair system of marine bacterial populations.

The second goal of this project is to determine how genetic effects caused by pollutants relate to observed ecological effects. To accomplish this goal we will examine: (1) the extent to which microbial activity and productivity are affected by introduced pollutants; (2) the impact of pollutants on bacterial community structures; (3) the effect on elemental cycling which may occur as a result of pollution stress; (4) the effect of photolysis and photooxidation on stress caused by introduced xenobiotics; and (5) the role of trophic interactions and suspended materials on toxic effects caused by xenobiotics.

EXPERIMENTS AND MODELING OF TURBULENCE/SEDIMENT/ PETROLEUM HYDROCARBON INTERACTION IN THE ESTUARINE WATER COLUMN

Gerhard H. Jirka
Leonard W. Lion
Monroe Weber-Shirk

The overall objective of the proposed research is to carry out controlled experimental studies leading to the development and verification of an advanced sediment/contaminant transport model. The proposed experiments and model simulations are intended to build on the existing foundation of underlying hydrodynamic physical transport and chemical transformation processes while maintaining a balanced level of attention to each of these disciplines.

Sorption on particulate matter is one of the dominant phase transfer processes affecting movement and fate of contaminants in the water environment. While other processes may govern specific chemical types (e.g. surface gas transfer for volatilizing hydrocarbons, or photochemical or microbial degradation) sorptive processes affect the widest range of contaminants, including the hydrophobic nonionic organic compounds contained in petroleum hydrocarbons.

Once dissolved materials are sorbed their fate is intimately linked to the transport of the particulate matter itself, or "...if we know the pathways of the sediments, we know the pathways of other contaminants" (Lick, 1982). In the coastal and estuarine environment, a number of phenomena with a wide range of time and spatial scales are important in determining the particle movement, including the detailed hydrodynamics (turbulence) of the water body, the flocculation and aggregation mechanisms among particles in the presence of salinity gradients, the depositional/erosional interaction between water and bed, eventual biochemical degradation, etc.

Water quality management in the estuarine zone, including assessment of the impact of spills, remediation of contaminated sediment areas, and location of sensitive facilities, requires the implementation of sophisticated predictive techniques that capture not only the overall hydrodynamic circulation and transport patterns but also the local details of the turbulence/ sediment/ contaminant interactions within the water column., Existing estuarine models available to the decision-maker are severely limited in that they often contain inaccurate or grossly averaged formulations of the physical/chemical fundamentals, or they lack proper balance (e.g. stressing hydrodynamic details while oversimplifying chemical processes), or they are not verified due to lack of appropriate field or laboratory data.

Given the manifold interactions between hydrodynamic and physical/chemical processes a controlled study is required in which equal attention is given to both transport processes and contaminant biogeochemistry. We propose to conduct the following

detailed investigations:

(1) A laboratory simulation using a Differential Turbulence Column (DTC) to study, in a simulated vertical estuary column, the interaction between estuarine turbulence, vertical ionic gradients, and sediment and contaminant types, in particular, petroleum hydrocarbons. The experiment will be designed to have independent, and spatially and temporally variable, control of all process time scales so that the salient characteristics of actual estuarine conditions can be simulated, while enjoying the sampling convenience, detailed insight, and data reliability of a laboratory setting.

(2) The development of a transport model that includes the detailed physical and chemical process kinetics governing particle interaction and contaminant sorption in the turbulent estuarine water column. This formulation will be based on the detailed insight gained from the DTC simulation as well as other available experimental data from more conventional experiments (e.g. batch, reaction kinetic experiments and simple settling tanks).

ANAEROBIC OXIDATION OF HYDROCARBON CONTAMINANTS IN MARINE AND ESTUARINE SEDIMENTS

Derek R. Lovley

The overall objective of this research is to understand the role of anaerobic microbial metabolism in the degradation of hydrocarbon contamination in harbor sediments. The two most potentially important processes, sulfate reduction and Fe(III) reduction, will be investigated. We will test the hypotheses that Fe(III) reduction is an important, previously unrecognized, pathway for hydrocarbon oxidation and Fe(III) availability is a major factor limiting the rate of hydrocarbon degradation in contaminated sediments.

Objective 1.

Determine whether there are Fe(III)-reducing microorganisms which can degrade petroleum hydrocarbons in contaminated estuarine and marine sediments.

Hypotheses

(1) In accordance with our previous finding of monoaromatic hydrocarbon-degrading Fe(III)-reducers in freshwater aquatic sediments and aquifers, there are also marine and estuarine Fe(III)-reducing microorganisms that are capable of degrading monoaromatic hydrocarbons.

(2) Thee is a previously unrecognized capacity for Fe(III)-reducing microorganisms to degrade polyaromatic and aliphatic hydrocarbon components of petroleum.

Objective 2.

Compare the pathways and relative rates of hydrocarbon oxidation by Fe(III)-reducing and sulfate-reducing communities in estuarine and marine sediments.

Hypotheses

(1) Whether Fe(III) or sulfate is the terminal electron acceptor for hydrocarbon oxidation, hydrocarbon contaminants are oxidized directly to carbon dioxide without the production of extracellular intermediates.

(2) When Fe(III) is available, Fe(III) preferentially serves as the electron acceptor for hydrocarbon degradation.

(3) Hydrocarbon contaminants are degraded faster with Fe(III) as an electron acceptor than with sulfate. Therefore, addition of insoluble Fe(III) oxides to bottom sediments is a feasible mechanism for stimulating removal of hydrocarbon contaminants from harbor sediments.

Objective 3.

Isolate hydrocarbon-oxidizing Fe(III)- and sulfate-reducing microorganisms and characterize their physiology in order to learn more about the factors controlling the rate and extent of anaerobic hydrocarbon oxidation in sediments. These microorganisms will also serve as models for the future development of molecular probes with which to study the structure of hydrocarbon-degrading communities.

DIGESTIVE KINETICS DETERMINES BIOAVAILABILITY OF POLLUTANTS

Lawrence M. Mayer

Any fundamental understanding of the exposure of organisms to pollutants via digestive uptake must be based on the physiology of that exposure. The measurement of contaminant concentrations in various media has long been dominated by empirical or artificial chemical methods. We propose to begin assessing the ability of organisms to remove pollutants from sediments, using the digestive means of the organisms themselves as the analytical extractants, as well as time constants relevant to actual feeding conditions. Our overall programmatic goals, therefore, is the **determination of the bioavailability of pollutants as a function of the digestive constraints and potentials of organisms.** We will focus on deposit feeders exposed to sediment-bound pollutants as our model system.

We have three specific objectives in this study:

(1) **Measure that fraction of various pollutants in sediments available to solubilization in the guts of various deposit-feeding animals, relative to concentrations detected by standard analytical methods.** This objective would provide direct demonstration, we anticipate, of the small fraction of many pollutants that can be solubilized during a gut passage and hence potentially taken up by the organism. These analyses would allow assessment of variability of the fraction of pollutant that is bioavailable among different animal-sediment-pollutant combinations. Time courses will reveal the time dependence of pollutant solubilization within the context of various digestive strategies and will help define feeding guilds of animals that are variably susceptible to pollutant uptake.

(2) **Determine the "active agents" responsible for pollutant solubilization within guts, and use these findings to guide exploration of the chemical nature of pollutants on sediment particles.** What types of enzymes, surfactants, and other chemical characteristics of gut juices are responsible for pollutant solubilization? We will pay particular attention to the ability to solubilize lipoidal materials. An important spinoff of this work may be the ability to design in vitro measures of bioavailable pollutant concentrations, using commercially available reagents such as enzyme preparations. We anticipate variable taxon-specific "cocktails" to be universally relevant, but our work with a variety of pollutant-organism-sediment combinations will permit assessment of the feasibility of such an approach.

(3) **Test the hypothesis that patterns of pollutant availability in sediment are similar to patterns of nutrient availability.** Does optimal selection of food resources (e.g., at recruitment, particle selection, or digestive strategy scales), which has positive implications for animal success, also maximize exposure to pollutants? We expect this hypothesis to be true for some pollutant-organism-sediment combinations and not true for others. We will examine the correspondence between bioavailable food and pollutant concentrations at various scales.

THE RELATIONSHIP BETWEEN COPPER SPECIATION AND CYANOBACTERIA DISTRIBUTION IN HARBORS AND OTHER COASTAL ENVIRONMENTS

James W. Moffett
Larry Brand

Copper is important in marine environmental quality because it is toxic to marine organisms and is present at elevated levels in many coastal waters through its use as an antifouling agent. The micronutrient and toxicological properties of copper are controlled by its speciation. Copper speciation is controlled by its complexation with naturally-occurring organic ligands. This influences its toxicological properties because complexed copper is much less toxic than the free Cu^{2+} ion. There is considerable variability in Cu speciation in seawater because complexation is dominated by a very strong chelator or class of chelators which shows considerable spatial and temporal variability.

We propose to study the relationship between Cu speciation and Synechococcus in several coastal environments to evaluate the importance of Cu in marine ecosystems. Synechococcus has been chosen as the organism of primary focus for the following reasons:
(1) It is the most Cu sensitive organism studied by Brand in his comprehensive survey of Cu toxicity to marine phytoplankton. As such, it may be an indicator of Cu stress in aquatic environments.
(2) It is very important in marine ecosystems. For instance, it contributes up to 50% of overall primary production in the Sargasso Sea.
(3) Moffett has observed that a correlation exists between Synechococcus abundance and the concentration of strong chelators in the Sargasso Sea. We have demonstrated that Synechococcus produces strong chelators in culture with comparable binding constants to the compounds found in the water column, possibly to reduce Cu toxicity.

Our study will address the following questions:
(1) Is there a correlation between Synechococcus distributions and Cu speciation, in coastal waters where the dynamic range in Cu speciation is even greater than the upper water column of the Sargasso Sea? In particular, is this true between developed harbors and pristine environments?
(2) Do strains of Synechococcus isolated from high Cu environments show higher resistance to Cu toxicity indicating adaptation?
(3) Do cultures of Synechococcus produce the ligand in response to Cu toxicity? Does production increase with increasing Cu?
(4) Can the answers to 1-3 be used to invoke some kind of feedback mechanism which regulates Cu speciation and Synechococcus?
(5) Can our results be used to set criteria for acceptable levels of Cu input into localized environments which will not affect the phytoplankton community?

SPECIATION AND REACTIVITY OF TOXIC METALS IN ANOXIC SEDIMENTS

John W. Morse

The primary objective of the proposed research is to investigate the influences of metal speciation on the kinetics of toxic metal solid phase transitions and interactions between solid phases and natural waters. Primary emphasis will be on the metals As, Cd, Co, Cu, Hg, and Zn and sulfidization-desulfidization reactions associated with near-interfacial anoxic sediments and overlying waters.

Within this general objective specific sub-objectives are:

(1) to experimentally determine the rates at which different chemical species of metals react under conditions approximating those found in anoxic sediments

(2) to determine if metals are at elevated levels, in chemically-reactive forms, in ship berthing and harbor areas

(3) to determine the extent to which metals have become associated with authigenic pyrite and the rate of this process

(4) to determine the rate of metal release to oxic waters when near-interfacial anoxic sediments are resuspended.

MATHEMATICAL MODELS RELATING THE EFFECTS OF XENOBIOTIC SUBSTANCES ON INDIVIDUALS AND POPULATIONS

Roger M. Nisbet

The broad objective of this research is to develop mathematical models suitable for relating the effects of xenobiotic substances on individuals and populations of benthic marine organisms. The importance of this aim derives from the fact that while management of marine environmental quality demands understanding of long-term effects on populations of plants and animals, much experimental information relates only to short-term effects on individuals. The models have the potential to link the large body of physiological information on individual responses to the less accessible, but fundamental, issues of population dynamics and demography.

We propose to develop testable, individual-based populations models applicable to benthic marine organism. While developing the methodology, we shall concentrate on one ecologically important genus (the mussel Mytilus) for which sufficient empirical data are available at different levels of biological organization to permit powerful tests of models incorporating hypothesized processes. Later in the grant period, we shall test the generality of insights obtained from research on mussels by constructing models of other marine species for which less data are available.

From a survey of the literature on the effects of xenobiotic substances on mussels, we concluded that the research must start with a model of the acquisition and allocation of energy by individual organisms and its allocation to maintenance, storage, growth and reproduction. We have previously developed such a model; after some model testing and refinement, we propose to use the model in the following studies:

(1) prediction of the individual response to toxicant exposure if short-term changes in rate processes of exposed organisms (commonly measured in terms of "scope for growth") are assumed to persist. This work will use data from (at least) one metal, organic, and organometal toxicant.

(2) identification of appropriate p' iological variables to enable us to relate "acute" response (what is commonly measured) to "acclimated" response)the important quantity at the population level).

We expect that this energetics model will generalize to other organisms. By the end of the project, the model will be a well-tested tool, ready for practical application.

The second theme of our research is to model population dynamics in a spatially complex environment, using techniques developed by Dr. W.G. Wilson, the proposed post-doctoral researcher in the project. In preparation for this work, we shall study simplifications of the energetics model that retain the key responses to toxic substances, but omit as much detail as possible.

We shall then conduct two major modeling studies with the following aims:

(1) to predict the effects of environmental change on a small patch of mussels (area a few m^2). This model will include both physical and physiological stresses on the animals.
(2) to relate the effects on small spatial scales to those at larger scales (e.g. km of coastline).

The first of these population studies is tightly focused, and we shall again deliver a well-tested, carefully coded model, applicable to other organisms and xenobiotics. The endpoint of the second study is much more open, but will include insights on the problems of "scaling up" in space in the context of well-defined, practical issues.

NEW MATERIALS FOR HEAVY METAL REMOVAL IN MARINE HARBORS

Mehran Pazirandeh

The objective of this research program is to utilize genetic engineering and recombinant DNA technology to develop high affinity materials for large-scale, cost-efficient removal of heavy metals and radioactive compounds from point source discharges and for marine harbor remediation. Novel metal-binding peptide sequences will be designed and generated based on existing metal binding proteins and through the screening of millions of randomly-generated peptide sequences (random peptide library technology). A further objective is to produce large quantities of various metal-binding peptide polymers in bacteria and to target these polymers to the cell surface for use as a biosorbent. In addition to providing a collection of novel metal-binding peptides for various applications including bioremediation, the characterization of these metal-binding peptides will address fundamental questions regarding the metal-binding sites of proteins and the structure/sequence motifs that constitute such sites, which will allow for the rational design and synthesis of peptide sequences with tailored affinities to specific metal or radioactive compounds. Furthermore, research on protein-targeting to the bacterial cell surface will provide further insight into the mechanism of translocation of proteins across membranes.

ESTUARINE COLLOIDS: SORPTION CAPACITY, COLLOID-FACILITATED TRANSPORT AND BIOAVAILABILITY

Peter H. Santschi
Gary A. Gill
Mark C. Benfield

(1) Identify the significance of colloidally-mediated transport of trace elements and metalloids to organisms; particularly whether sequestration of trace metals and metalloids into colloids acts to reduce bioaccumulation processes by lowering bioavailability.

(2) Characterize the physico-chemical characteristics of estuarine colloidal matter to absorb trace elements and metalloids. Of particular interest is the sorption capacity and active surface site concentrations of colloidal material with respect to major compositional differences. SorPtion studies will be conducted based on classification of solution metal ions into: type A (e.g. Al(III), Th(IV)), methyl-Hg(II), and Ag(I), and metalloids (e.g., Se, As, Ge). These studies will be designed to identify how metal and metalloid associations with colloidal matter change as a function of major variables in estuarine systems, such as suspended matter and iron concentration, dissolved organic carbon (DOC), salinity, carbonate, and pH.

(3) Determine the bioavailability and toxicity of colloidally-bound trace elements and metalloids to shrimp. Of interest here is whether the nutritional quality of colloids is affected by the presence of trace element contaminants. In particular, are these colloidal trace elements less available to biota, as is the case for particulate metals, or are they at times more available, as is the case for B-metals complexed by low-molecular-weight organic molecules?

(4) Identify whether bioavailability of colloids to shrimp is related to the hydrophobicity of the organic complex, or if there are steric and kinetic reasons why some colloidal forms of trace elements are less bioavailable.

(5) Investigate whether it is possible to identify the bioavailable fraction of colloidal trace elements using: 1) simple digestion treatments, such as weak acid leaches or mild reducing agents; and 2) through correlations with the concentrations of Fe, Al, N and S.

(6) Determine if the earliest feeding larval stages (protozoeal larvae) of penaeid shrimp are capable of utilizing colloidal material as a nutrient sources.

(7) Determine if colloidally-complexed heavy metals, metalloids and organics accumulate more rapidly than uncomplexed forms.

(8) Identify where colloidally-bound trace elements and metalloids are sequestered within the shrimp.

BIOLOGICAL MEDIATION OF MATERIAL FLUXES ACROSS THE SEDIMENT-WATER INTERFACE IN ESTUARIES AND COASTAL SYSTEMS

Linda C. Schaffner
L. Donelson Wright
Jerome Maa

We propose to examine the relative importance of biological, physical and chemical processes in controlling the fluxes of particles, fluids and contaminants across the sediment-water interface in the benthic boundary layer. As a result of these processes and their interactions, contaminants may be recycled many times before they are buried or transported from an ecosystem. The resultant increased contaminant residence time has important implications for estimating ecosystem effects because it influences chemical partitioning and degradation/transformation processes. Specific questions we will address include: 1) How do benthic organisms and boundary layer flows interact to recycle sediments prior to burial? 2) How do benthic organisms and boundary layer flows interact to determine the distribution of fluids within sediments and flux across the sediment-water interface? 3) At what length and time scales are these processes important for contaminant transport and fate?

The series of hypotheses that will govern our investigations are developed from our conceptualization of biological, physical and chemical process interactions in the benthic boundary layer of estuarine and coastal systems with fine sediment beds. These are outlined below:

(1) In areas where bioturbation and bioirrigation are low or non-existent (e.g. because of severe pollution stress or rapid sediment accumulation, or during winter), particle and fluid transport and fate at the sediment-water interface will be dominated by physical processes, but potentially modified by microbial processes, especially sediment binding.

(2) In areas dominated by small, shallow-dwelling, "opportunistic" organisms (e.g. many estuarine and coastal regions stressed by moderate pollution, moderate rates of sediment accumulation, or low salinity), both biological and physical processes will influence particle and fluid transport and fate at the sediment-water interface. The length scales over which most biological processes operate will be constrained by organism size. Physical sediment reworking, erosion and deposition will determine the final fate particles, because the depth of physical bed reworking will exceed the depth of biological reworking. However, under "average" conditions, organism activity at the sediment-water interface can be quite high. Therefore, short-term fluxes of sediments and fluids will be controlled by biological, as well as by physical processes.

(3) In areas dominated by diverse communities that include "equilibrium"-type species (e.g. some high salinity estuarine regions and physically-quiescent coastal areas not impacted by significant pollutant stress), biological processes will strongly govern the fluxes, transport and fate of particles and fluids at the sediment-water interface. Depth of mixing by bioturbation and bioirrigation will exceed physical reworking depths except under the most extreme conditions (e.g. some storms). Although the rates and magnitudes of sediment and fluid exchange will be controlled primarily by biologically-mediated processes, physical processes are likely to enhance these effects.

(4) The biogeochemical processes controlling material transport in the benthic region vary on spatial and temporal scales. While macroscale (e.g. physical-advective) processes are most likely to affect spatial distribution of contaminants, short-term (e.g. chemical-diffusive) activities will probably regulate biological effects. Diffusive transport will be dependent upon the physical-chemical properties (e.g. hydrophobicity) of the contaminant. Furthermore, we expect biological processes (e.g. bioturbation, bioirrigation) in areas of high productivity to influence both physical and chemical transport processes.

POTENTIAL FOR THE DESTRUCTION OF SHIPBOARD OILY WASTES BY ANAEROBIC MICROORGANISMS

Joseph M. Suflita

The discharge of oily wastes at sea is prohibited by international agreement and innovative technologies for the on-board destruction of such materials are required. It may be that oily wastes can be biologically treated so that overboard discharges are not considered environmentally damaging. Therefore, this proposal focuses on two interrelated needs of the Navy: 1) the need to evaluate the potential for biological methods leading to the management of shipboard oily wastes and, 2) the need to predict the transport and fate of hydrocarbon pollutants and their degradation products in marine environments. These needs will be addressed by systematically examining the metabolic fate of various classes of oily hydrocarbons in relation to the predominant processes governing the flow of carbon and energy in marine anaerobic environments. Such a study will allow the Navy to predict the kinds of hydrocarbons that are subject to anaerobic decay and to identify the pertinent environmental factors serving to limit or stimulate these bioconversions. This information can be used by the Navy for risk assessment and help provide a scientific foundation for the evaluation of biotechnological approaches for the destruction of shipboard oily wastes. Implementation of this proposal will generate reliable information on the potential for hydrocarbon degradation under anaerobic conditions, the requisite microorganisms, the metabolic pathways they employ, the catabolic enzymes involved, and, conceivably, their regulation.

RESIDENCE TIME OF PARTICLE-REACTIVE POLLUTANTS IN THE COASTAL SEA BED: CONTROL BY RESUSPENSION AND SEA BED MIXING PROCESSES

Donald Swift

Burial modified by resuspension

Toxic pollutants entering estuarine and coastal waters are known to preferentially associate with the particulate phases, and their dispersal is therefore controlled by the natural cycle of fine sediment transport. Prediction of the final fate of toxic pollutants released into the marine environment therefore requires a detailed understanding of the dynamics of fine sediment dispersal. Phases of sediment dispersal, involving burial in the sea floor, are the most poorly understood, yet are liable to have a major effect on the fate of pollutants. Sediment burial in shallow marine environments is strongly modified by resuspension in response to wind-and wave-driven currents during storms, to peak tidal currents, and to river flooding. The effects of these events are to cycle the sediment repeatedly between the sea floor and the water column as dispersal proceeds.

Burial modified by mixing

Burial is also modified by sediment mixing induced by burrowing organisms. In this process, contaminants are moved downwards into the sea bed by biodiffusion when they first accumulate. However, as burial proceeds and the sediment cover thickens, contaminants are also moved back up towards the surface where they re-enter the dispersal system. The final fate of a contaminated particle in a shallow marine dispersal system will depend on the relative rates of sea floor accumulation versus resuspension and mixing in the sea bed. Our goals are therefore 1) to fully reveal the mechanics of these processes, 2) to develop techniques for measuring their rates, and 3) to develop a capability for predicting scenarios of pollutant dispersal in shallow marine sea beds.

EFFECTS OF EPISODIC DISTURBANCES ON MICROBIAL DEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN COASTAL SEDIMENTS

Gordon T. Taylor
Glenn Lopez

It is well known that microbially-mediated degradation and mineralization of polycyclic aromatic hydrocarbons, PAHs, are relatively slow in most marine sediments. PAHs tend to accumulate in fine-grained, organic-rich sediments in coastal and estuarine environments. The rate of microbially-mediated degradation is controlled by the availability of molecular oxygen and a few select other terminal electron acceptors (e.g. NO_3). The preponderance of coastal marine sediments are anoxic when undisturbed. Oxidation of PAHs in these anoxic sediment layers, however, can be brought about in two ways. In the first, anoxic pore waters are exchanged with overlying oxic waters; this can be effected by ventilation by benthic animals. The second way is to advect buried sediment into oxic waters. This can be accomplished by physical resuspension or by bioturbation. These processes are discontinuous and increase the contact time of oxygen with sediment microbes and affect the redox-potential gradient and distribution of other electron acceptors. The effects of sediment cycling between oxic and anoxic conditions on microbial processing of PAHs is virtually unknown. Furthermore, the role of alternative bacterial pathways, such as denitrification or methanogenesis, on PAH degradation, known to be somewhat important in terrestrial and microcosm systems, have not been evaluated for marine systems.

The overall objective of this project is to understand the physicochemical and biological processes that control degradation and mineralization of PAHs in coastal marine sediments. Specifically, we will examine how the natural processes of physical resuspension and bioturbation, which result in episodic sediment mixing and ventilation, affect microbiological processing of PAH-contaminated sediments. We wish to better comprehend how physical and macrobiological forcing functions affect remobilization of PAHs and their degradation products and affect microbially-mediated PAH degradation and microbial community metabolism, productivity, biomass, and composition in coastal sediments. A further goal is to better understand and model the role of selected benthic infauna in stimulating PAH-degrading microbial populations. We will examine several infaunal species that represent several functional groups, including active ventilators, weak ventilators, surface deposit feeders, and head-down deposit feeders.

BINDING AND TRANSPORT OF METAL IONS

Jeffrey D. Winkler

This proposal describes basic research directed towards the reversible, real-time, in situ binding and release of metal ions. Specifically, a photochemically-driven system has been developed in our laboratory that has been successfully applied to the transport of copper and zinc ions across an organic membrane. The key to this technology is the reversible opening and closing of a spiropyran nucleus, 1->2, which functions as the photochemical antennae in the dynamic system that we have developed.

The specific goals of this work during the proposed grant award period are to achieve highly selective binding of a variety of metal ions and to significantly increase the on/off rates of metal ion binding in the systems that we have previously described. Outlined herein is the design and synthesis of new metal ion carriers as well as the optimization of the transport apparatus.

THE ROLE OF ANAEROBIC MICROBIAL PROCESSES ON THE BIODEGRADATION OF FUEL COMPONENTS IN ESTUARINE SEDIMENTS

Lily Y. Young
Junko Kazumi

The intent of the proposed research is to determine the degradative capacity, with an emphasis on the novel anaerobic processes, of sediment microbial communities with respect to their ability to utilize the BTX (benzene, toluene and xylene) components of petroleum fuels. From this effort, it is anticipated that the restorative capacities of an estuarine ecosystem can be evaluated, and the contributions of the different groups of anaerobic microorganisms can be determined. It is further anticipated that the activity of the natural microbial community can be understood and can be enhanced and/or exploited under certain circumstances to reduce the contaminant load on the ecosystem.

The specific objectives of the proposed research are:

(1) To determine the predominant anaerobic microbial processes occurring in anoxic sediments of a hypereutrophic estuary, and to compare the relative importance of the various microbial processes in anoxic sediments which differ in salinity and organic input.

(2) To identify the anaerobic microbial processes of environmental significance in the biodegradation of the BTX components of fuels.

(3) To examine the effect of BTX components singly, and in mixtures, on degradation rates by natural sediment microbial communities under different reducing conditions since BTXs often occur as contaminant mixtures in the environment.

IN SITU MEASUREMENT AND SPECIATION MODELING OF COPPER IN THE MARINE ENVIRONMENT

Albert Zirino
Stuart L. Belli

(1) To develop speciation methods for Cu in marine (estuarine) waters based on combined potentiometric and voltammetric criteria - principally Cu-ion selective electrode potentials (Cu-ISE) and stripping polarograms (SP). Because both of these methods are adaptable to in situ use, one objective is to ultimately make the measurements in situ and to provide a means of performing near-real-time environmental monitoring.

(2) To provide a measurement protocol for Cu ion and labile Cu in marine waters, including calibration with Cu-ion activity buffers and current-voltage scans using stripping polarography and develop a theoretical framework for interpretation of the analytical result in the context of the sample matrix. The theoretical framework will be in the form of a combined organic/inorganic chemical speciation model and will be based on both thermodynamic (potentiometric) and kinetic (voltammetric) parameters.

(3) To correlate the newly-developed speciation criteria to marine bacterial cell toxicity as measured with MICROTOX and to determine the ability of Cu-ISE to predict toxicity in marine waters.

Attachment C

ENVIRONMENTALLY SOUND SHIPS

Thrust Areas

Shipboard Waste Conversion FY93-$2212K, FY94-$1775K, FY95-$1912K
The development of an efficient plasma arc pyrolysis system for destruction of aqueous wastes and the use of anionic detergents for oil-water separation; the study of combustion control in shipboard incinerators and the development, for use in incinerators, of metal-ceramic compounds that can withstand extremely high temperatures.

Membrane Technology FY93-$1071K, FY94-$972K, FY95-$1032K
The design of polymers for membrane filters (used in oil-water separators) that have minimal fouling and improved permeability.

Non-Emission Refrigeration FY93-$1987K, FY94-$1397K, FY95-$1709K
The development of efficient, cost-effective thermoelectric and thermoacoustic cooling systems to replace the current CFC-based ones in ships and aircraft.

Environmentally-Sound Coatings FY93-$905K, FY94-$346K, FY95-$334K
The development of a paint that contains no volatile organic compounds and of a hull coating with nontoxic, antifouling properties.

In Situ, Real Time Sensors FY93-$900K, FY94-$900K, FY95-$900K
The development of novel types of sensors for use in monitoring toxic substances in shipboard waste streams.

Clean Naval Power Plants FY93-$700K, FY94-$700K, FY95-$700K
The reduction of NOx, CO and UHC in large, marine gas turbine and diesel engines.